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(54) ALIPHATIC PERFLUORO COMPOUNDS AS WETTING AGENTS IN PHOTOGRAPHIC MATERIAL CONTAINING GELATINE

(71) We, CIBA-GEIGY AG., formerly CIBA Limited, a Body Corporate organised according to the Laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a light-sensitive photographic material and to a process for its manufacture. It especially relates to the use of surface-active substances as auxiliary agents when coating films and papers with gelatine-containing light-sensitive layers and gelatine-containing auxiliary layers. Possible light-sensitive layers are preferably silver halide-containing layers, whilst possible auxiliary layers are backing layers, substrata, intermediate layers, covering layers, filter layers and transfer layers.

It is usual to add surface-active substances to photographic gelatine solutions in order to assist the uniform wetting of film, paper or layers which already cover these supports. The wetting of the finished cast layers by processing baths is also intended to be assisted by surface-active substances in the layers. Numerous surface-active agents have already been proposed as additives to the casting solution, for example, saponin and also a large number of synthetic anionic, cationic and non-ionic substances.

The demands made on surface-active substances are very diverse. They must be obtainable in a quality which always remains constant, which is not the case for natural products such as saponin. They must be photographically harmless and must not have any disadvantageous effect on the sensitivity, gradation, haze and storage life of the photographic emulsions. They must be compatible with emulsion additives, for example, hardeners, sensitisers, coupling agents and dyestuffs. Furthermore they must improve the physical properties of the casting solutions to a sufficient extent in order to fulfill their purpose; that is to say, they must make uniform castings possible, which are free from streaks, repelled material (comets) and foam (small bubbles), and which adhere well to the substrate. At the present time especially high demands are made of such surface-active compounds since thinner layers and higher casting speeds are constantly being adopted, with a further aim being to cast layers without waiting for the drying of the previously cast layers.

In particular, the manufacture of uniform layers for the silver dyestuff bleaching process presents difficulties, since the casting solutions contain water-soluble azo dyestuffs which undergo mutual interactions with the gelatine and hence unfavourably influence the flow properties of the casting solutions.

The present invention is based on the observation that perfluorinated aliphatic compounds as hereinafter defined of non-ionic or anionic character can advantageously be employed as wetting agents in photographic, gelatine-containing, casting solutions, with a much better uniformity of the applied layers being attainable than is possible with the wetting agents usually employed in photographic processes.

The present invention thus provides photographic material which contains a water-soluble, surface-active, non-ionic or anionic, aliphatic perfluoro compound as hereinafter defined as a wetting agent in at least one gelatine-containing layer.

The present invention further provides a process of making photographic material according to the invention, wherein at least one gelatine-containing solution which contains a water-soluble, surface-active, non-ionic or anionic, aliphatic perfluoro compound as hereinafter defined as a wetting agent, is cast on a support.

The gelatine-containing layer, in the photographic material of the invention, may additionally contain a water-soluble azo dyestuff for the silver dyestuff bleaching process. This layer is essentially free from faults, for

example streaks and small bubbles.

Preferably, the aliphatic perfluoro compounds to be used as wetting agents in accordance with the invention correspond to the formula (1)

$$R_F—Z \qquad (1)$$

wherein

R_F represents the radical $Y—(CF_2)_n—$ in which Y represents hydrogen or fluorine and n is an integer of at most 9 preferably of from 3 to 9 and

Z represents an optionally further-substituted carboxylic acid or sulphonic acid radical, an acyloxy radical of the formula

$$—O—OC—R_F \text{ or } —O—OC—R_4$$

wherein R_F has the meaning given above and R_4 is as defined hereinafter, or an acyloxyalkyl radical of the formula

$$—CH_2—O—OC—R_5$$

wherein R_5 is as defined hereinafter.

Thus the perfluoro compounds are preferably perfluorinated aliphatic carboxylic acids, sulphonic acids, carboxylic acid-amidocarboxylic acids, sulphonic acid-amidocarboxylic acids or the salts of these acids, or sulphonic acid amides, carboxylic acid amides, carboxylic acid esters, urethanes, esters of perfluoroalcohols with aliphatic carboxylic acids, perfluoro esters of perfluorinated aliphatic carboxylic acids of formula (10) below or perfluoro esters of aliphatic carboxylic acids of formula (9) below. Further possibilities are also perfluorophosphoric acid esters. By perfluoro compounds are meant compounds which are fluorinated as completely as possible, that is to say compounds which apart from an optionally further substituted functional group and an optional terminal hydrogen atom, a so-called ω-H, exclusively contain fluorine atoms as substituents. The compounds having an ω-H are also called ω-H-perfluorinated compounds.

Anionic or anion-active perfluoro compounds for example correspond to the formulae

(2) $R_F—CO—O—X$

(3) $R_F—SO_2—O—X$

(4) $R_F—CO—N(R_2)—R_1—CO—O—X$

and above all

(5) $R_F—SO_2—N(R_2)—R_1—CO—O—X$

wherein R_F has the meaning given above, R_1 represents an alkylene radical, R_2 represents a hydrogen atom or an alkyl radical and X represents a hydrogen atom or an alkali metal atom.

Non-ionic perfluoro compounds for example correspond to the formulae

(6) $R_F—SO_2—N(R_2)(R_3)$

(7) $R_F—CO—N(R_2)(R_3)$

(8) $R_F—CO—O—R_4$

(9) $R_F—O—OC—R_4$ and

(10) $R_F—O—OC—R_F$.

wherein R_F and R_2 have the meanings given above, R_3 represents a hydrogen atom or a substituted alkyl radical and R_4 represents an alkyl radical.

By substituted alkyl radical R_3 is meant an alkyl radical substituted by a hydroxymono- or hydroxypolyethylenedioxy radical of the formula $—O—(CH_2CH_2O)_p—H$ wherein p is an integer of at most 10, or an acyloxy radical of the formula $—O—OC—R_4$ wherein R_4 has the meaning given above.

Preferred representatives of the formulae (2) to (5) for example correspond to the formulae

(12) $R_F—CO—O—Me$

(13) $R_FSO_2—O—Me$

(14) $R_F—CO—N(R_5)—(CH_2)_m—CO—O—Me$

and especially

(15) $R_F—SO_2—N(R_5)—(CH_2)_m—CO—O—Me$

wherein R_F has the meaning given above, R_5 represents a hydrogen atom, a methyl group or an ethyl group, m represents an integer having a value of 1 to 6 and Me represents an alkali metal atom.

Preferred representatives of the formulae (6) to (10) for example correspond to the formulae

(16) $R_F—SO_2—N(R_5)—(CH_2)_m—O—(CH_2CH_2O—)_p—H$

(17) $R_F—SO_2—N(R_5)—(CH_2)_m—O—OC—R_4$

(18) $R_F—CO—N(R_5)—(CH_2)_m—O(CH_2CH_2O—)_p—H$ and

(19) $R_F—CO—O(CH_2CH_2O—)_p—H$

wherein R_F, R_4, R_5 and m have the meanings given above and p represents an integer having a value of at most 10.

Of especial interest are perfluorinated carboxylic acids, their alkali metal salts or esters of perfluoro-alcohols with aliphatic carboxylic acids. These perfluoro compounds correspond to the formulae

(20) $F—(CF_2)_n—CO—O—X$

(21) $H(CF_2)_n—CO—O—X$

(22) $F(CF_2)_n—CH_2—O—OC—R_5$ and

(23) $H(CF_2)_n—CH_2—O—OC—R_5$

wherein X, R_5 and n have the meanings given above. Preferably n is 7 or 8.

An especially suitable wetting agent corresponds to the formula

(24) $F_3C—(CF_2)_7—SO_2—N<\begin{matrix}CH_2—COOK\\CH_2—CH_3\end{matrix}$

Wetting agents of formulae (1) to (10) and (12) to (24) are commercially available and are for example sold by Minnesota Mining and Manufacturing Company as "FC"-types e.g. ammonium salts of perfluorocarbonic acids such as FC 126 (anionic) and salts of perfluoroalkylsulfonic acids such as FC 95 (anionic), FC 98 (anionic), and by Messrs. E.I. du Pont de Nemours and Company under the name "Zonyl S", e.g. Zonyl S 13, a phosphoric acid ester.

The wetting agents to be used in accordance with the invention are employed in concentrations of 0.05 g to 5.0 g per kg of ready-to-cast solution, preferably in amounts of from 0.2 g to 1 g. The photographic properties such as sensitivity, gradation and haze are not influenced by the perfluorinated wetting agents.

The wetting agents to be used in accordance with the invention can also be employed together with other known non-perfluorinated surface-active compounds, for example saponin. Gelatine-containing solutions which contain the wetting agents to be used in accordance with the ivention are not only suitable for the application of a single layer but especially also for the simultaneous application of several layers according to the cascade casting process, as is described in United States Patent Specification No. 3,005,440. Instead of a simultaneous application of several layers it is also possible to manufacture a multi-layer laminate by applying one layer after the other onto the same support, either by using a wet-on-dry process or by using a wet-on-wet process.

The wetting agents of the type "FC" or "Zonyl S" used in the Examples which follow are products of Messrs. Minnesota Mining and Manufacturing Company and Messrs. E.I. du Pont de Nemours and Company, respectively.

The following Examples illustrate the invention:—

Example 1

A photographic silver halide-gelatine emulsion containing 25 g of silver as silver bromide with 2.5 mol % of silver iodide and 40 g of gelatine per kg of emulsion is cast on a substrated transparent cellulose triacetate substrate, with the commercial product "FC 128" of probable formula (24) being added as the wetting agent in various amounts within the range of 0.05 g to 3.0 g per kg of ready-to-cast solution. All layers are free from faults and are uniform. A sensitometric examination shows no difference in sensitivity, gradation or haze.

Similar results are obtained with the commercial products "FC 126 (anionic), FC 95 (anionic), FC 98 (anionic), FC 170 (non-ionic), FC 176 (non-ionic) and Zonyl S 13" (phosphoric acid esters) mentioned above.

Example 2

A photographic silver halide gelatine emulsion and an aqueous gelatine solution as a protective layer are simulaneously applied to a transparent cellulose triacetate substrate with the aid of the cascade casting process, as described in United States Patent Specification No. 3,005,400. The silver halide-gelatine

emulsion contains 0.5 g of "FC 128" of probable formula (24), and the gelatine solution contains 2.0 g of "FC 128" per kg of casting mixture. The resulting product is free from streaks and other casting faults.

EXAMPLE 3

A silver bromide-iodide emulsion is manufactured which contains 30 g of gelatine, 13 g of silver as silver bromide with 2.5 mole % of silver iodide and 2.4 g of a blue-green dyestuff according to British Patent Specification No. 1,042,300, in 1000 g of aqueous solution. The silver halide is sensitised towards red light in the usual manner.

One half of the emulsion is cast on a transparent cellulose triacetate substrate, with 0.3 g of sodium diisobutylnaphthalenesulphonate per kg of casting solution being used as the wetting agent. The other half of the emulsion is cast on the same support, with the addition of 0.3 g of "FC 128" of probable formula (24). Both layers are exposed behind a grey wedge and are developed in a *p*-methylaminophenolsulphate-hydroquinone developer.

The following results are obtained:

Wetting Agent	Haze	Sensitivity rel. log. units	Gradation
with sodium diisobutylnaphthalenesulphonate	0.02	3.22	0.58
with "FC 128"	0.02	3.22	0.58

Furthermore, a 1 metre long piece of both cast films is fixed without exposure, cut into 35 mm wide strips, and the colour density of these strips measured at intervals of 6 mm at a time. The mean value of the colour density and the standard deviation are calculated for both cast films from the measured values:

Wetting Agent	Mean value of the colour density	Standard deviation
with sodium diisobutylnaphthalenesulphate	2.00	0.324
with "FC 128"	1.98	0.076

From this it can be seen that the layer containing "FC 128" is much more uniform that the layer containing sodium diisobutylnaphthalenesulphonate.

Explanation:

$$\text{Standard deviation } S=\sqrt{\frac{\epsilon(x-x_m)^2}{n-1}}$$

x_m = mean value
x = measured values
n = number of measured values

EXAMPLE 4

The following layers are successively applied to a transparent polyethylene terephthalate substrate:

1. A silver halide-gelatine emulsion sensitised to red light, containing a blue-green image dyestuff according to British Patent Specification No. 1,042,300.
2. A gelatine layer.
3. A silver halide-gelatine emulsion sensitised towards green light, containing a purple image dyestuff according to British Patent Specification No. 914,876.
4. A gelatine layer.
5. An unsensitised silver halide-gelatine emulsion containing a yellow image dyestuff according to British Patent Specification No. 1,094, 956.

0.035% of "FC 128" of probable formula (24) are in each case added as the wetting agent to the ready-to-cast aqueous solutions.

In a comparison experiment, the same solutions using 0.035% of sodium diisobutylnaphthalenesulphonate were cast.

Samples of both materials are fixed, washed and dried. All colour densities lie between 2.5 and 2.8.

Two other samples of these materials are hazed by homogeneous exposure, developed in *p* - methylaminophenolsulphatehydroquinone developer, soaked, bleached in a colour bleaching bath, soaked, freed of excess silver in a

bleach fixing bath, soaked and dried. A strip of 1 metre length and 35 mm width was cut from each of these two samples and the colour densities were measured at intervals of 6 mm. The following values are thus obtained:

Wetting agent	Mean values of the analytical colour densities			Standard deviations of the analytical colour densities in ENDT-units x10^{-3}		
	yellow	purple	blue-green	yellow	purple	blue-green
sodium diisobutylnaphthalene-sulphonate	1.20	0.97	1.17	88	19	108
"FC 128"	1.08	1.02	1.24	32	21	26

It can be seen from this Table that after photographic processing the material containing "FC 128" is again more uniform than the material containing sodium diisobutylnaphthalenesulphonate. (In the table "ENDT" refers to "equivalent neutral densities transmission").

WHAT WE CLAIM IS:—

1. Photographic material which contains a water-soluble, surface-active, non-ionic or anionic, aliphatic perfluoro compound as hereinbefore defined as a wetting agent in at least one gelatine-containing layer.

2. Photographic material as claimed in Claim 1, wherein the gelatine-containing layer contains a water-soluble azo dyestuff as well as a perfluoro compound.

3. Photographic material is claimed in Claim 1 or 2, wherein the gelatine-containing layer contains a perfluoro compound of formula (1)

$$R_F—Z \qquad (1)$$

wherein

R_F represents the radical $Y—(CF_2)_n—$ in which Y is hydrogen or fluorine and n is an integer of at most 9, and Z represents an optionally further-substituted carboxylic acid or sulphonic acid radical, an acyloxy radical of the formula $—O—OC—R_F$ or $—O—OC—R_4$ wherein R_F is as defined above, and R_4 represents an alkyl radical, or an acyloxyalkyl radical

$$—CH_2—O—OC—R_5$$

wherein R_5 represents hydrogen, methyl or ethyl, as wetting agent.

4. Photographic material as claimed in Claim 3, wherein the gelatine-containing layer contains a perfluoro compound of formula

$$R_F—SO_2—N(R_2)—R_1—CO—O—X$$

wherein R_F has the meaning given in Claim 3,

R_1 represents an alkylene radical,

R_2 represents a hydrogen atom or an alkyl radical and

X represents a hydrogen atom or an alkali metal atom, as the wetting agent.

5. Photographic material as claimed in Claim 4, wherein the gelatine-containing layer contains a perfluoro compound of formula

$$R_F—SO_2—N(R_5)—(CH_2)_m—CO—O—Me$$

wherein R_F has the meaning given in Claim 4,

R_5 represents a hydrogen atom or a methyl or ethyl group,

m represents an integer of from 1 to 6 and

Me represents an alkali metal atom, as the wetting agent.

6. Photographic material as claimed in any one of Claims 1 to 5, wherein the perfluoroalkyl moiety R_F represents the radical

$$Y—(CF_2)_n—$$

wherein n represents an integer of from 3 to 9, and Y is as defined in claim 3.

7. Photographic material as claimed in Claim 5 or 6, wherein the gelatine-containing layer contains the perfluoro compound of formula

$$F_3C—(CF_2)_7—SO_2—N<\begin{matrix}CH_2—COOK\\ CH_2—CH_3\end{matrix}$$

as the wetting agent.

8. A process of making photographic material according to claim 1, wherein at least one gelatine-containing solution which contains a water-soluble, surface-active, non-ionic or anionic, aliphatic perfluoro compound as hereinbefore defined as a wetting agent, is cast on a support.

9. A process as claimed in Claim 8, wherein a gelatine-containing solution which in addition to the perfluoro compound contains a water-soluble azo dyestuff, is cast on a support.

10. A process as claimed in Claim 8 or 9, wherein a perfluoro compound of formula (1) defined in Claim 3 is used as the wetting agent.

11. A process as claimed in claim 10, wherein a perfluoro compound of the formula defined in Claim 4 is used as the wetting agent.

12. A process as claimed in Claim 11, wherein a perfluoro compound of the formula defined in Claim 5 is used as the wetting agent.

13. A process as claimed in any one of Claims 10 to 12, wherein a perfluoro compound having the R_F moiety as defined in Claim 6 is used as the wetting agent.

14. A process as claimed in Claim 12 or 13, wherein the perfluoro compound of the formula as defined in Claim 7 is used as the wetting agent.

15. A process as claimed in Claim 8, conducted substantially as described in any one of the Examples herein.

16. Photographic material whenever prepared by a process claimed in any one of Claims 8 to 15.

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